

DECOMPOSITION TECHNIQUE FOR BHC UNDER VACUUM

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Introduction

Large amount of POPs (Persistent Organic Pollutants) related agrichemicals are now prohibited to use and they are buried underground. However, it is seriously concerned that those buried POPs still have a potential for causing a soil contamination.

We have been developing a technique for removing dioxins in fly ash or contaminated soils by heating under vacuum¹⁻³, since it is carried out in a closed system and thus this procedure is safe for the people working at the plant and/or living near them.

Employing our pilot scale equipment for vacuum heating technique, we have decomposed about 1.5 kg of Hexachlorocyclohexane(BHC, 97% in purity), and 1.5 kg of chlordan. As a result, BHC and chlordan are completely decomposed by this process respectively. Chlorine molecules dechlorinated from BHC are trapped in the alkali reactor, which is filled with CaO and maintained at 1123 K, and forming CaCl₂.

Methods and Materials

A pilot plant carries out this experiment is designed for remediating POPs contaminated objects such as soils and fly ash. In this equipment, the object to be treated is heated under vacuum, and the gaseous fraction is processed in the pumping line. In this study, we have applied this technique for decomposing agrichemicals such as BHC. In the heating chamber, 1.5 kg of BHC (1,2,3,4,5,6-Hexachlorocyclohexane, 97 % γ -BHC) are buried within the 50 kg of matrix. In this experiment, soils once processed at 1073 K under vacuum are used as a matrix to hold the BHC. This heating chamber is connected to the pumping line having vacuum pumps. Between the heating chamber and the vacuum pump, a buffer chamber, an alkali reactor and a condenser are connected in line. About 48 kg of processed soils as in the heating chamber are also filled in the buffer chamber. A function of the buffer chamber is to control an emission rate of gaseous fraction to the pumping line. By employing this buffer, the vacuum heating technique is applicable not only for the inorganic objects but also for the organic rich objects. Total amount of alkali (CaO) filled in the alkali reactor is 201 kg. The condenser intervened between the alkali reactor and the vacuum pump is cooled by liquid Nitrogen. All the lines through the heating chamber to the cold trap are made of steel.

Before heating the BHC and the matrix, the alkali reactor is heated up to 1123 K. After the alkali reactor is reached 1027K, then the heating chamber is heated to 1073 K and maintained for 4 hours at the temperature. Gaseous fraction emitted from BHC during the process is passed through the buffer chamber and the heated alkali reactor. The gaseous fraction from the alkali reactor is cooled in the condenser.

After the experiment, analysis are made at the various points of the equipment including residue of the BHC and matrix, soils in the buffer, alkali, condenser, and exhaust gases. Not only γ -BHC, but α -BHC, β -BHC, δ -BHC, PCDDs, PCDFs, and Co-PCBs, are analysed by HRGC/HRMS SIM. Analysis are carried by Shimadzu Tech. Research Co., Ltd.

For chlordane sample processing, the same manner is applied. In the 1.5 kg of sample, 7.4 % of chlordane (cis-chlordane: 4.1 %, trans-chlordane: 3.3 %) is included. For chlordane experiment, cis-chlordane and trans-chlordane are analysed.

Results and Discussion

Amount of BHCs in the equipment after the experiment are shown in Figure 1. As shown, all measured BHC isomers are not detected in respective points. Detection limits for the residue, the buffer soils, and alkali are $<0.0001\text{mg/Kg}$. The detection limit for the cold trap is $<0.00002\text{mg/L}$, and for the exhaust gases is $<0.0000005\text{mg/m}^3$. Therefore by the vacuum heating, BHC is substantially decomposed and substantially no BHC isomers is synthesised.

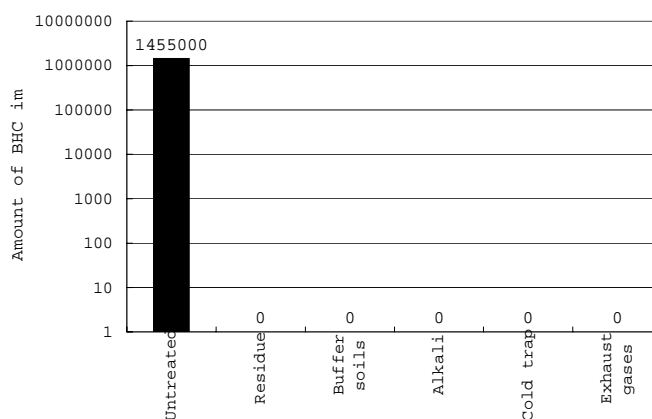


Figure 1. Amount of BHC in the equipment before and after the vacuum heating process.

		PCDDs/PCDFs	Co-PCB	TotalDioxins
Untreated (51.5kg)	pg-TEQ /g	0	0	0
BHC (1.5kg)	ng-TEQ /g	0	0	0
Matrix (50kg)	pg-TEQ /g	0	0	0
Residue (49kg)	pg-TEQ /g	0.43537	0.00009	0.44
Buffer soils (48kg)	pg-TEQ /g	1.8591	0.00024	1.9
Alkali1 (10kg/41kg)	pg-TEQ /g	0	0.00094	0.00094
Alkali2 (10kg/39kg)	pg-TEQ /g	0	0.00034	0.00034
Alkali3 (10kg/40kg)	pg-TEQ /g	0	0.00076	0.00076
Alkali4 (10kg/40kg)	pg-TEQ /g	0	0.00052	0.00052
Cold trap (6.707L)	pg-TEQ	129.7	37.1118	170
Exhaust gases (11.498m ³)	ng-TEQ /m ³	0.0009539	0.001924182	0.0029

Table 1. DXNs (Tetra-Octa chlorinated) concentration in the equipment before and after the vacuum heating process.

The dioxins(PCDDs, PCDFs, and co-PCBs) concentrations in the experiment after the experiment are shown in Table 1. Initially, no dioxins are detected from the BHC sample. Therefore, by the vacuum heating process, small amount of dioxins are formed although BHC

is completely decomposed. However, except the cold trap, the concentrations of synthesised dioxins in respective fraction are sufficiently low. This cold trap is employed for the reason that we would like to detect all the fraction emitted from the alkali reactor, and as a result, almost all Dioxins in the gas are condensed in the trap during the process. The pressure in the pilot plant is maintained 0.5-200 Pa through the processing. Therefore, if the gas fraction from the alkali reactor is emitted to the atmosphere, the dioxins concentration would be much lower than the regulation level. In the actual situation for this process, any filter such as bag filter or charcoal filter may be equipped after the vacuum pump for promoting safety.

In the alkali reactor, only non chlorinated dibenzo-furan (DF) is detected though Tetra-Octa PCDDs/PCDFs are not detected. Figure 2 and Figure 3 shows amounts of PCDD/PCDF homologue which remained in alkali reactor after processing BHC and chlordane, respectively. Smaller chlorinated congeners are remained in alkali. A knowledge that the dechlorination reaction of dioxins occur in the vacuum heating process¹⁻³ is confirmed in these two experiment for other POPs. In this BHC decomposition experiment, dibenzo-furan is detected but not dibenzo-para-dioxin(DD). Also, neither Mono-Tri, and Tetra-Octa chlorinated PCDFs nor PCDDs are remained in the alkali reactor. Different from the BHC, DD, DF and Mono-Di chlorinated PCDDs/PCDFs are remained, when the chlordane is processed (Figure 3.). Observed of congeners pattern suggests the different decomposition pathways are existing for the BHC and chlordane. Also, corresponding to the chemical characters of BHC and chlordane, the local pressure profile in the vacuum chamber seems different, and this may cause a local dependence where the BHC or chlordane are mainly decomposed. However, we are now planning to study those decomposition mechanism in vacuum condition.

Conclusion

We have already demonstrated that by vacuum heating process, dechlorination/hydrogenation (DCH) reactions as well as destruction reactions of dioxins are proceeded². Different from the DCH reaction started from OCDD, almost of all dioxins

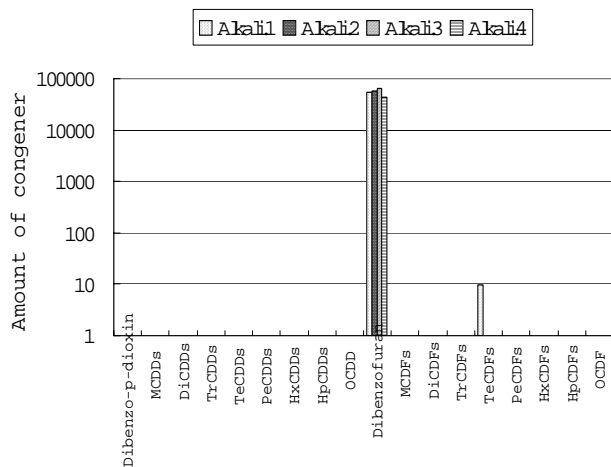


Figure 2 : Amounts of PCDD/DF homologue remained in alkali reactor processing BHC

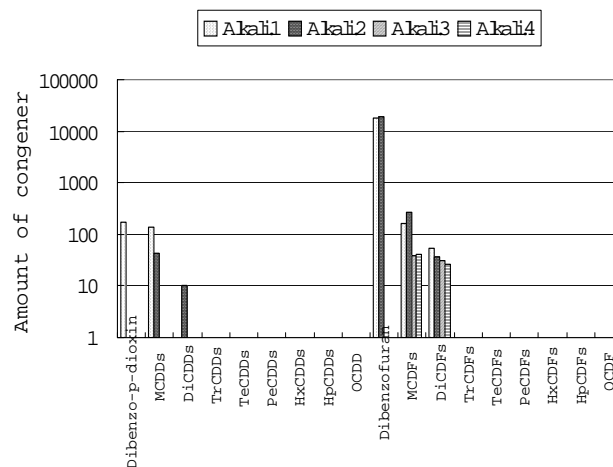


Figure 3 : Amounts of PCDD/DF homologue remained in alkali reactor processing chlordane

remained are formed from BHC through the process. When dioxins are synthesised in vacuum state, it is suggested that PCDFs are more preferably formed than PCDDs. Since the mean free path in vacuum is longer than the one in ambient condition, two oxygen molecule hardly react with dioxins precursors to form PCDDs. From Fig.2 and 3, less chlorinated PCDDs/DFs are dominant in the alkali reactor. This shows that synthesised dioxins are dechlorinated in the pumping line including alkali reactor.

In this study we have applied the vacuum heating technique to the agrichemicals such as BHC or chlordane. Observed pressure profiles are so different from the one when we processed contaminated soils and the fly ash in the same system. In fact, total amount of organic compounds are not so large in the soil sample. On the other hand, BHC and chlordane are almost 100% organic, and this cause larger the pressure dynamic range when processing agrichemicals. Therefore, one meets difficulty in controlling pressure in the vacuum chamber when heated agrichemicals. Thus, we employed the soil matrix and the buffer soils to moderate temperature and the pressure change in the chamber. Those matrix and buffer play a roll as a filter or valve which is capable of controlling the amount gaseous fraction emitted to the pumping line. Otherwise it is difficult to maintain the vacuum condition and to process a large amount of gaseous fraction from the organic compounds in the alkali reactor. To maintain a vacuum state in the chamber and the pumping line is so important in this method, those described inorganic matrix is useful. By using those inorganic matrix such as soils, we made the vacuum heating technique applicable for processing BHC, chlordane, and the other POPs related organic-rich objects such as agrichemicals. Also, employing this technique, one can decomposing agrichemicals with surrounding soils as is, which may be contaminated with dioxins.

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